# Polyelectrolyte Materials – Reflections on a Highly Charged Topic

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## 1 Polyelectrolytes

Polyelectrolytes are polymers having a multiplicity of ionizable groups that generally cause them to be water-soluble. When in solution, they dissociate into polymeric ions and numerous small ions, known as counterions.[1] The counterions tend to remain in the region of the polymeric ions because of electrostatic attraction, a phenomenon known as ion binding. There are numerous pieces of experimental evidence for ion binding, such as the measured tendency of cations to travel in the same direction as a polyanion in an electric field.

In aqueous solution, the molecules of a polyelectrolyte can take up a number of conformations, because rotation of the bonds making up the polymer backbone is reasonably unhindered. This ease of rotation makes polyelectrolyte molecules flexible.

The size and shape of the conformation depends on the state of neutralization of the polyelectrolyte. When the charge on the polymer is low, *i.e.* at low or zero degrees of neutralization, the polymer adopts a compact coil shape. As neutralization proceeds, and the charge on the polymer increases, electrostatic repulsion causes the conformation to change. The compact coil unfolds, and at high levels of neutralization, adopts an expanded rod-like conformation. Poly(acrylic acid), for example, with a degree of polymerization of 1000, adopts a coiled conformation at its natural pH that is essentially spherical and has a radius of 20 nm. At full neutralization, it becomes a rod with a maximum extension of 250 nm[2]. Changes of this kind affect the solution viscosity, which for the practical materials described in the current article has a profound effect on properties such as film formation or measured setting times.

This review is particularly concerned with two sets of materials of growing technical and commercial importance, namely waterborne paints and polyelectrolyte cements for various medical applications. Here, we are less concerned with the complicated physical chemistry of polyelectrolytes and their solutions than with the practical aspects of how functional materials can be fabricated from these polymers having the necessary properties of integrity, adhesion, and/or strength.

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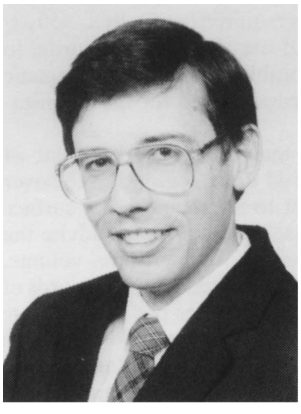


### 1.1 Polyelectrolytes and Water

The key property of polyelectrolytes is their ability to dissolve in water. Water, though, is an unusual solvent for polymers, and some of its features need to be considered briefly.

Water is unique in being the only inorganic liquid to occur naturally on earth; it is also the only substance which can be found naturally in all three physical states, solid, liquid, and vapour.[3] It is the most readily available solvent, and, in principle, the least expensive. Yet its physical properties are very different from those of organic solvents. Its surface tension, boiling point, latent heat of evaporation, and density are all very high both in comparison with other solvents, and for its very small molar mass. Details of these physical properties, together with those of other common organic solvents used in industry, are given in Table 1.[4]

The reason that so many of these values of physical constants are anomalously high for water is that its molecules are highly associated. This associated nature arises from hydrogen bonds between adjacent molecules which in turn occur because of the high polarity of the water molecule.

We know from simple observations that, when it comes to solvents, like dissolves like, *i.e.* polar solvents dissolve polar (including ionic) substances, while non-polar solvents dissolve non-polar substances. Water being highly polar therefore dissolves polar and ionic compounds.

Polymers are usually non-polar. Polyelectrolytes, by contrast, are more or less polar in character, *i.e.* they contain some monomer units bearing polar or ionizable functional groups (See Table 2).

Where it can be done, neutralization of ionizable groups in a polymer will improve the strength of the hydrophilic attraction, hence improve the water-solubility. For example, the copolymer of acrylic acid (89%) and methyl acrylate (11%) is not water-soluble as such, but becomes so on neutralization with sodium hydroxide.[5]

**Table 1** Physical properties of water and other solvents

| Property | Water | Mineral spirits | Acetone | Xylene |
|---|---|---|---|---|
| Molar mass | 18 | 170 | 58 | 106 |
| Boiling point/°C | 100 | 214.5 | 56.5 | 144 |
| Flash point/°C | — | − 12 | − 95 | − 25 |
| Latent heat of evaporation at bp/kJg$^{-1}$ | 2.259 | 0.481 | 0.565 | 0.39 |
| Dipole moment /debyes | 1.84 | 0.0 | 2.88 | 0.4 |
| Density/g | 1.00 | 0.752 | 0.787 | 0.86 |
| Dielectric constant | 78 | 1.83 | 21.3 | 2.37 |

**Table 2** Polar monomers for water solubility/dispersibility

| Monomer | Functional group | Structure |
|---|---|---|
| 'Vinyl alcohol' | Hydroxyl | $-(CH_2-CH.OH)-$ |
| Acrylic acid | Carboxylic acid | $-(CH_2-CH.CO_2H)-$ |
| Acrylonitrile | Nitrile | $-(CH_2-CH.CN)-$ |

### *1.1.1 Hydrophobic Interactions*

So far, the discussion of solubility has been limited to a consideration of the attractive forces involved. But the polymers used do not necessarily experience only attractive forces. They generally have hydrocarbon backbones, which are insoluble in water. It is only the polar functional groups that confer water solubility/dispersibility. Hydrocarbon backbones are hydrophobic, and there is thus a hydrophobic contribution to the interaction between the polymer and water. To understand how this hydrophobic interaction manifests itself we need to consider some simple thermodynamics.

Energetically, hydrocarbons and water are attracted to each other, as thermochemical measurements demonstrate. The enthalpy change, $\Delta H$, is negative. However, hydrocarbons are none the less insoluble in water. This is because the free energy, $\Delta G_{\text{solution}}$ is against the process, *i.e.* it is positive. From the Gibbs equation,

$$\Delta G_{\text{solution}} = \Delta H_{\text{solution}} - T\Delta S_{\text{solution}}$$

it follows that the $T\Delta S_{\text{solution}}$ term, and hence $\Delta S_{\text{solution}}$ itself, must be negative. This in turn shows that the entropy of the final state (the proposed aqueous solution of hydrocarbon) has decreased relative to the initial, two-phase state. In other words, the proposed solution is more ordered than water itself. This result is attributed to the formation of an ordered cage structure of water molecules around the hydrocarbon molecule in which water has fewer degrees of freedom than in pure water itself.

In liquid–liquid phase diagrams, the hydrophobic interaction results in a lower critical solution temperature, and in the remarkable result that raising the temperature reduces the solubility (Figure 1a). In general, solution behaviour represents a balance between the hydrophilic and hydrophobic nature of the macromolecule. This may result in so-called 'closed solubility loops' (Figure 1b), in which the lower temperature behaviour and lower critical solution temperature arise due to hydrophobic effects, while at higher temperatures, solution behaviour becomes dominated by hydrophobic effects.

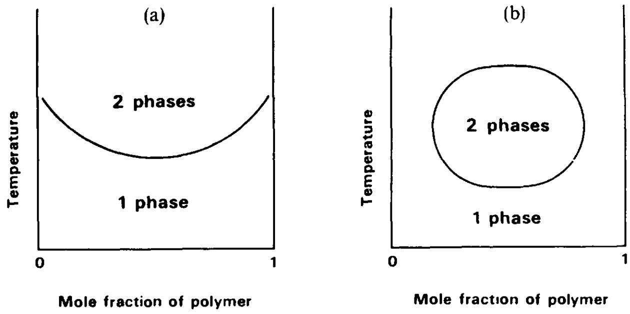


**Figure 1** Two possible phase diagrams for polyelectrolyte/water systems with significant hydrophobic interactions. (a) Solution behaviour of water-soluble polymer exhibiting a lower critical solution temperature only. (b) Solution behaviour of water-soluble polymer showing closed solubility loop in which lower-temperature behaviour is dominated by hydrophobic interactions and higher-temperature behaviour by strong hydrophilic effects.

## 2 Waterborne Coatings

Waterborne coatings are becoming increasingly widely used because they cause reduced environmental impact compared with traditional solvent-borne paints. Though of long history, the main impetus for their development is usually seen as the beginnings of environmental awareness in the late 1960s, a trend which has continued ever since in the industrialized world. The first significant piece of legislation was the Los Angeles 'Rule 66', passed in July 1966 and aimed at reducing emission of a range of volatile organic compounds (VOCs) into the atmosphere.[6] Among the main VOCs controlled by this legislation were alkenes, aromatics, and branched-chain ketones, all of which are constituents of conventional low-solids solvent-borne paints. The major concern with these compounds was that they are photochemically active; in the special circumstances of the geographical location of Los Angeles, solvent vapours did not readily disperse, but lingered and concentrated, with their photochemical reactions leading to the formation of severe smogs. Concern with such solvents was not confined to Los Angeles and by 1980, all of the US states had individual regulations similar to those of Rule 66.

This environmental concern is by no means restricted to the USA. European countries, too, have enacted legislation controlling VOC emissions over the last decade or so.

While this relatively benign effect on the environment is the main advantage of waterborne coatings, it is by no means the only one. Others are listed in Table 3.

**Table 3** Advantages of waterborne coatings

(i) Reduced risk of fire
(ii) Reduced exposure of the workforce to potentially damaging organic vapours
(iii) Easier waste disposal
(iv) Liquid, therefore can use conventional application methods, *e.g.* spraying

If water were the ideal paint solvent, no technologist would ever use anything else. Clearly, it also has disadvantages for this purpose. These are listed in Table 4.

**Table 4** Disadvantages of waterborne coatings

(i) A tendency for films to remain water-sensitive
(ii) Greater energy needed for drying due to high latent heat of evaporation of water
(iii) Humidity affecting on drying rates
(iv) Flash rusting on ferrous substrates
(v) Difficulty in wetting greasy surfaces

Hayward[7] has also pointed out that there is a tendency to assume that the water is of negligible cost. This is not always the case and in many countries the cost of obtaining water of sufficient purity may exceed that of using the alternative organic solvents. Water must be available not only in large quantities and reliably, but also of consistent quality. For many coating applications, deionized water has become the standard carrier liquid, with very low conductivities required (typically 1—50 $\mu$s/cm) depending on the proposed end-use of the paint. In order to obtain water of such quality, potable water free of organic matter and suspended solids is needed as feed for the deionization unit.

Water quality also has to be maintained at the point of disposal. The Water Act of 1985 laid down legislation to cover the control of discharge of effluent to rivers and other surface waters. Factories discharging aqueous effluent must advise the authorities on the nature, composition, temperature, volume, and rate of discharge. They must keep comprehensive records of discharges and must ensure that effluent does not contaminate specified underground water. The manufacture of waterborne coatings inevitably generates aqueous effluent, and care must be taken that the environmental advantages at the application stage are not lost at the point of waste disposal.

## 2.1 Electrodeposition

One of the major industrial uses of polyelectrolytes is in painting by electrodeposition This is the technique of applying coatings by means of an electric current The substrates must allow the passage of the electric current and hence function as electrodes In order to use polyelectrolytes in this way, solvents of high dielectric constant are needed, which in practice means the use of water In addition, since the article to be coated (the workpiece) must be capable of acting as an electrode it must be (a) metallic and (b) previously uncoated Consequently the process is restricted to that of priming (*i e* initial coating) of metal components In practice this is not an undue limitation, and large volumes of bulky items such as car bodies are routinely primed in this way Indeed, it is now the only method of priming of car bodies used industrially

The commercial development of electrodeposition began in the early 1960s In fact, however, the technology had existed in embryo form since 1919, when the first patent was granted for the coating of conductive articles using electric current [8] Later fundamental work was done on the deposition of latex paints, and on coatings for the interiors of metal cans [9] Despite this early work it was not until 1964, in a classic paper, that Finn and Mell[10] described in detail a viable industrial process for electrodeposition using acceptable paint formulations The process was used for priming car bodies, an application which still represents the largest use of electrodeposition technology

The original version of the process, as described by Finn and Mell,[10] used anodic deposition That is to say, the paint resins were negatively charged, the polymers generally bearing ionized carboxylic acid functional groups to confer mobility in the electric field In turn, the workpiece being coated was made the anode in the coating bath Nowadays, however, cathodic deposition has become more widely used In this process, the workpiece is the cathode of the coating bath and the resins are positively charged, typically with amino functional groups By the mid 1980s, the change to cathodic deposition for priming automobile bodies was virtually complete

Cathodic deposition offers a number of advantages over anodic deposition as an industrial coating technique These include better corrosion resistance at low film thicknesses and high deposition rate per unit of current (so-called 'good throwing power')

An important change needed in altering the technology from anodic to cathodic deposition is that the counter-electrode in the cathodic process must be inert in order to prevent it becoming oxidized Typical counter-electrodes used are graphite or stainless steel By contrast, in anodic electrodeposition, mild steel is acceptable as the counter-electrode

### *2 1 1 Physical Chemistry of Electrodeposition*

Electrodeposition consists essentially of two steps, (i) the movement of the charged polyelectrolyte molecules towards the test piece under the influence of the electric field, so-called electrophoresis, and (ii) insolubilization at the electrode This latter step covers a complex sequence of events and typically occurs because the steps taken to solubilize the polymer are reversed For example, as we have seen, carboxylic acid polymers are more soluble when neutralized, the extreme case being that they are insoluble in their acid form and only soluble when neutralized Under the influence of the electric current, the polyanion travels to the anode, dragging with it a high proportion of counterions These counterions become expelled from the polymer as they get close to the anode, at which point the polymer becomes insoluble and is deposited

Similar arguments apply for the more common process of cathodic deposition Polycations are typically solubilized by species such as quaternary ammonium salts, and they too become insoluble at the electrode In this case, insolubilization occurs because solubilizing counterion reacts with the excess of hydroxyl ions present in the vicinity of the cathode to generate the less soluble tertiary amine groups [11]

$$NR_2H^+ + OH^- \rightarrow NR_2 + H_2O$$

In fact there is a preliminary step to the whole electrodeposition process, namely the establishment of a diffusion boundary layer at the metal surface [12] Fundamental studies using a rotating disk as the electrode have shown that this diffusion boundary layer takes a finite time to form, and that until this layer is established, a coherent film cannot be laid down [12]

Commercial coating processes use well-defined conditions, *i e* potential difference of at least 80 V and current density of at least 1 mA/cm² Time of deposition is typically quite short, *i e* between 30 seconds and 4 minutes Under these conditions, the electrode reactions are effectively those of the electrolysis of water

$$\begin{array}{ll}
\textit{At the anode} & 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \\
\textit{At the cathode} & 4H_2O + 4e^- \rightarrow 2H_2 + 4OH^- \\
\hline
\text{Total reaction} & H_2O \rightarrow H_2 + \tfrac{1}{2}O_2
\end{array}$$

The cathode reaction generates twice as much gas by volume as does the anode reaction This seems important in determining the electrical resistance of the deposited film However, at each electrode the rate at which gas is generated is low, so that bubbles do not build up in the film Instead the gases are able to escape by simply dissolving in the electrolyte solution

Side-reactions may also occur, and these cause varying levels of metal compounds to be deposited within the film The effect of these side-reactions is illustrated by data given in Table 5

**Table 5** Comparison of films formed on different substrates[9]

| Substrate | Deposition | Metal content of film (%) | Coating weight (mg/Coulomb) |
|---|---|---|---|
| Iron | Anodic | 0 05 | 10 0 |
| Iron | Cathodic | 0 015 | 4 5 |
| Aluminium | Anodic | 0 037 | 14 3 |
| Aluminium | Cathodic | 0 200 | 3 2 |
| Nickel | Cathodic | 0 002 | 4 2 |
| Zinc | Cathodic | 0 094 | 4 0 |

Studies such as those from which these data were taken show that in anodic deposition, ferrous substrates such as mild or galvanized steel undergo side-reactions that contribute to the insolubilization processes This is undesirable because the products are coloured and discolour the deposited film

When the workpiece is removed from the deposition bath it has two coats, one the insoluble, electrodeposited film, the other a surface layer of still-soluble polymer, which is effectively a dip-coat over the top of the main one This soluble coating is generally removed by rinsing with water, after which the workpiece is stoved to bring about crosslinking of the electrodeposited film

Practical paints for priming consist not only of polymer but also of pigments and extenders, both of which must be deposited on the article being coated, and at roughly the same rate as the polymer If not, the composition of the coating bath will change with time and this in turn will change the composition of the paint being deposited In principle, ensuring the deposition of two dissimilar dispersions at equal rates is a formidable feat of physical chemistry Fortunately, in practice, trial and error can usually be relied upon to yield formulations that are able to deposit binder and pigment at about the same rates

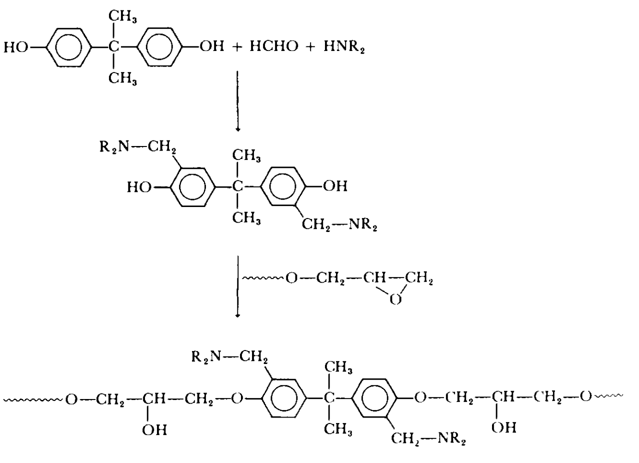
The reason that pigment particles move under the influence of the electric field is that molecules of binder tend to become adsorbed onto their surfaces [13] As a result of this adsorbed layer, the pigment particles travel in the same direction as the binder during electrodeposition, and arriving at the surface, retain their adsorbed layer of binder to become fully integrated into the coating On insolubilization, the pigment remains embedded in the organic coating

### 2.2 Other Waterborne Paints

Paints for application by electrodeposition are by no means the only type of waterborne coating available. There are the so-called 'emulsion paints' widely used domestically, which are actually made not from an emulsion at all, but from a latex, *i.e.* a stable dispersion of *polymer* in water. These, however, are not generally considered to be polyelectrolytes, even though industrial versions of them have been made and applied by electric current.

Other paints based on polyelectrolytes are the water-reducible systems.[14] They often contain a small proportion of organic solvent, to aid the dissolution process, but in sufficiently small amounts that the paint conforms to the regulations concerning VOC emissions. Typically, paints are made based on conventional solvent-soluble polymers that have been modified to confer water solubility, such as natural drying oils, alkyd resins, or epoxy systems. Modification generally involves introducing the kind of polar functional groups which we have already seen that confer water-solubility. Drying oils, for example, are reacted with maleic acid to introduce carboxylic acid groups. When applied to a substrate these coatings 'dry' mainly by the same process as the parent oil, *i.e.* by metal-catalysed reaction with atmospheric oxygen to lightly crosslink the film.

An alternative approach, used for epoxy resins, is to introduce amine groups using the so-called Mannich reaction (Scheme 1):



**Scheme 1** Mannich reaction for the preparation of water reducible epoxy resins.

Typically, practical paints based on these polyelectrolytes contain, in addition to pigment, a range of additives designed to improve flow and aid the drying process. For maleinized drying oils, these include the metal catalysts such as long-chain fatty acid salts of cobalt, manganese, and zirconium. Other additives, such as surfactants and thickeners aid wetting of substrates and stabilize the pigment dispersion. Lastly, for some polymers with carboxylic functional groups, volatile amines or even ammonia are used to enhance water-solubility. These are effectively additives and are lost by evaporation as the paint film dries, thus reducing the solubility of the film and making it less susceptible to disruption by moisture.

## 3 Dental and Medical Applications

Within the realm of healthcare applications, polyelectrolyte materials are mainly used in dentistry, though their use is spreading to branches of medicine, such as maxillo-facial and ear, nose, and throat (ENT) surgery. Two classes of polyelectrolyte material are available to clinicians, namely zinc polycarboxylate cements and glass-polyalkenoate (so-called 'Glass-ionomer') cements; this latter class includes light-curable versions.

Both classes fall into the category of acid–base cements.[15] Their setting involves reaction of acid groups on the polymer with powdered solid bases, either modified zinc oxide or aluminosilicate glass. These solids are bases in the sense that they are proton acceptors, even though they are not soluble in water.[1]

The zinc polycarboxylate cement was developed as a dental material by Smith in 1968.[16] In this first paper, the good adhesion to tooth materials and also the low irritancy of the material were highlighted. The zinc polycarboxylate cement is now widely used for such clinical procedures as lining cavities prior to placement of the main filling material, for attaching crowns to posts, and for the adhesion of orthodontic brackets as part of the treatment for misalligned teeth.

The components are a polycarboxylic acid, usually poly(acrylic acid), and a modified zinc oxide powder. The modified zinc oxide is prepared by mixing pure zinc oxide with small amounts of magnesium oxide and fusing the mixture at between 1100 and 1200 °C. This process reduces the reactivity of the zinc oxide towards the acid so that, in clinical use, the cement paste sets slowly enough to be mixed and placed. The heat treatment causes the zinc oxide to become slightly yellow in colour. This coloration is due to evaporation of oxygen to yield a non-stoichiometric substance corresponding to $Zn_{(1+x)}O$, where $x$ is less than or equal to 70 ppm.[17]

The zinc polycarboxylate cement sets rapidly to give a material, typical properties for which are given in Table 6. Not all of the zinc oxide reacts, so that, when set the cement consists of a zinc polyacrylate matrix with unreacted particles embedded in it as reinforcing filler.

**Table 6** Properties of zinc polycarboxylate dental cement[21]

| Property | Typical components/values |
|---|---|
| Liquid | 40—45% polyacid |
| Polymer | Usually poly(acrylic acid) |
| Powder:liquid ratio | 2.5—3:1 |
| Setting time/min | 2.5—4 |
| Compressive strength/MPa | 80—100 |

The setting process involves reaction of carboxylic acid groups with zinc oxide to form the zinc carboxylate units. The structure of these units is complex, with a range of types with subtly different chelating character being present as shown using FTIR spectroscopy[18] (see Figure 2). Covalent structures of this type are also known to occur in variety of monomeric zinc carboxylates.[19]

Despite the presence of these chelated zinc carboxylate structures, zinc polycarboxylate cements behave like thermoplastic

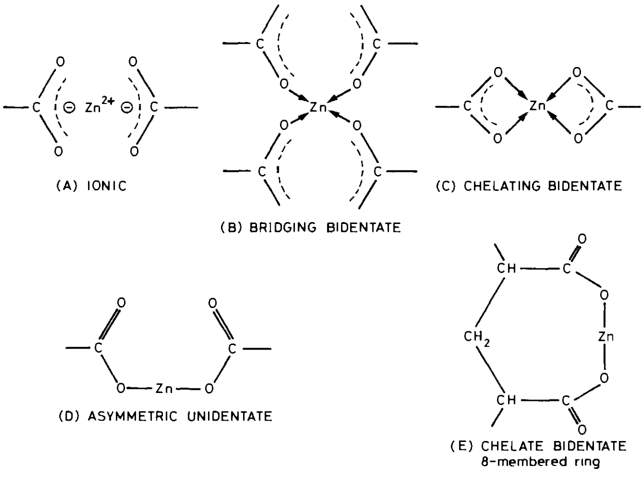


**Figure 2** Possible modes of bonding of zinc ions to carboxylate groups in zinc polycarboxylate dental cements.

composites, at least in terms of the effect of molar mass of the polyacid on fracture toughness [20] These results can be reconciled with the spectroscopic evidence for chelation if the covalent structures postulated are intramolecular rather than crosslinking

Water is retained in these cements when they set and it has a number of functions for these cements First, it is the solvent for the setting reaction, secondly, it is one of the products of the neutralization reaction between zinc oxide and poly(acrylic acid), and finally it occupies co-ordination sites around the metal ions, and hydration sites around the polyanion In addition it may also act as plasticizer, *i e* low molar mass component that reduces the rigidity of the bulk polymeric structure [21]

The invention of the glass-poly(alkenoate) dental cement occurred soon after that of the zinc polycarboxylate, and was achieved essentially by replacing zinc oxide with an aluminosilicate glass powder of the type used in the now obsolete dental silicate cement Initially, as for the zinc polycarboxylate, the acid used was poly(acrylic), but since this time, a variety of other acids have been employed, including poly(maleic) and acrylic acid/itaconic acid co-polymers [1]

Glass-poly(alkenoates) were given the trivial name 'Glass-ionomer', the name by which they still tend to be known to the dental profession These cements have more varied properties than zinc polycarboxylates, because the glass can be modified in a variety of ways to alter setting speeds and final properties However, like the zinc polycarboxylate, they set fairly rapidly with the inclusion of water to form materials that can be shaped and finished by the clinician Their uses include all those of zinc polycarboxylates, plus others such as gum-line cavity filling and so-called fissure-sealing between the cusps of teeth as a protective measure to prevent dental decay [22] Typical properties of glass-poly(alkenoates) are given in Table 7

**Table 7** Properties of glass-poly(alkenoate) dental cements[1]

| Property | Typical components/values |
|---|---|
| Liquid | 40—45% polyacid with up to 5% (+)-tartaric acid |
| Polymer | Poly(acrylic acid), poly(maleic acid) or itaconic/acrylic acid co-polymers |
| Powder liquid ratio | 2—3 5 1 |
| Setting time/min | 2 5—4 |
| Compressive strength/MPa | 160—180 |

Compared with zinc polycarboxylates, glass-poly(alkenoates) have improved opacity, hence can be used as restorations in the front teeth, where aesthetics is important They also release fluoride, since fluoride as $CaF_2$ is a constituent of the glass, and this protects the natural tooth material in the region immediately surrounding the glass-poly(alkenoate) restoration

Early on in their development a number of factors were identified that influence the speed of the setting reaction and the final strength of the cement These include molar mass of polymer, concentration of acid solution, powder liquid ratio, and the presence or absence of chelating agents, such as (+)-tartaric acid [22] In general, increasing all of these parameters except the concentration of (+)-tartaric acid reduces the setting time and increases the compressive strength of the set cement

Glass-poly(alkenoate) cements undergo gradual maturation processes that have no parallel in the setting of zinc polycarboxylates For example, compressive strength tends to increase gradually with time up to a maximum value The ratio of bound to unbound water also increases, this being defined as the ratio of water that may be removed by chemical dessication (*e g* by storage for 24 over silica gel at elevated temperatures) to that which remains in the cement during this treatment Zinc polycarboxylate experiences no real change in this ratio over a period of up to 6 months,[21] whereas glass-poly(alkenoates) show a significant increase in bound to unbound water over a similar period [1]

The setting reactions of glass-poly(alkenoates) are as follows

(i) Decomposition of the glass under the influence of the polyacid, leading to release of $Ca^{2+}$ ions and $Al^{3+}$ species, these latter probably being in the form of complex oxyanions containing several aluminium atoms [23]

(ii) Rapid reaction of the $Ca^{2+}$ ions with the polyacid chains, followed by slower reaction of $Al^{3+}$ species gradually released from the anionic complex

(iii) Gradual hydration of the inorganic fragments released in step (i) to yield a matrix of increasing strength and resistance to dessication [24]

These steps are illustrated in Figure 3

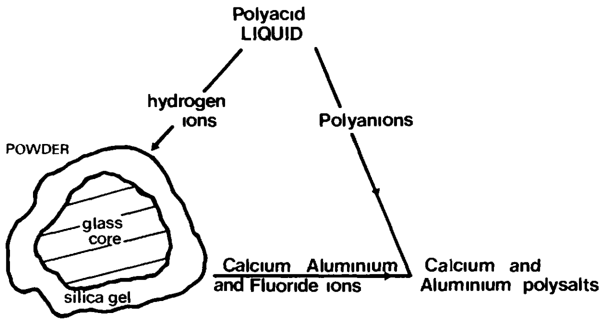


**Figure 3** Schematic representation of the setting of glass-polyalkenoate cements

Improvements in strength and wear properties of glass-polyalkenoates have been sought by such means as the inclusion of finely divided silver alloy or by fusing the glass with silver alloy prior to mixing, forming a ceramic–metal hybrid known as a cermet [25] The success or otherwise of these approaches is the subject of continuing research [25]

Another recent attempt to develop cements of this type has been to use the polymer poly(vinyl phosphonic acid) as the cement former [1] This carries the promise of improved clinical adhesion to tooth surfaces, and of better translucency than polycarboxylic acid cements These cements, which are not poly(alkenoates) but poly(phosphonates), are at an early stage of development, but initial findings concerning their properties are promising [1]

One disadvantage of glass-poly(alkenoates) is that they are sensitive to moisture in the early part of their life, soon after placement This may result either in washing out of still soluble species from the cement by saliva, or in patients who breathe through the mouth, in desiccation and inhibition of the setting reaction To overcome this sensitivity, clinicians tend to cover freshly placed cement with an impervious layer of varnish or petroleum jelly

An alternative approach has been the development of hybrid glass-polyalkenoates involving the incorporation of photopolymerizable components The resulting materials can be cured by irradiation with visible light They are very new, and have only become available within the past 3—4 years [26]

The use of photochemical means of curing limits the depth of individual layers of material that can be used because light can penetrate to only a given depth Such materials must therefore be used in thin layers (2 mm maximum) only This restricts their use to cavity lining or certain limited areas of restoration such as the edges of incisors

Light-cured glass-ionomers consist of a complex mixture of components These are (i) poly(acrylic acid) or a modified poly(acrylic acid), (ii) a photocurable monomer such as hydroxyethyl methacrylate, HEMA, or a photocurable side-chain grafted onto the poly(acrylic acid), (iii) an ion-leachable glass, and (iv) water Consequently, they set by a number of competing reactions to give complex structures

The initial setting reaction is the photochemical polymerization Depending on the precise details of the formulation, this process is either a co-polymerization of the HEMA with the polymer side-chains or homopolymerization of the functional groups in the side-chains Subsequently, the acid–base reactions typical of glass-poly(alkenoates) take place This process is designed to be slower than in conventional glass-poly(alkenoates), it is also probably impeded by the development of photopolymerized network and by the presence of organic molecules in the aqueous mixture

Very recently, these cements have been shown to exhibit properties of weak hydrogels, a feature attributed to the presence of HEMA in the cement [26] Cements allowed to mature dry for 24 hours were stronger in compression than those kept in water (70—80 MPa, compared with 50—60 MPa for those in water) More significantly, those stored in water had become plastic rather than brittle, and had swollen by between 3 and 5%, an expansion that might prove significant given the close tolerances required for filling materials in clinical dentistry These are new materials, though, and should not be written off because of disadvantages with the earliest commercial products Improvements to them are highly likely, given the intense research currently going into their development

Recently, glass-poly(alkenoate) cements have begun to be used outside dentistry Following the discovery of their excellent biocompatibility when in direct contact with bone, cements are being studied for a variety of surgical uses, including in orthopaedic surgery for fixing artificial joints,[1] in oral and maxillofacial surgery, for repairing damaged regions of bone, and in ear, nose, and throat surgery, for repair of the chain of ossicles in the inner ear and for fixing cochlea implants in place [27] These materials thus seem to have an exciting future in wider fields of medicine, as well as in dentistry The scope for tuning their properties by subtle changes in the chemistry of their constituents, coupled with their excellent biocompatibility, makes them likely to become materials of choice for a variety of clinical procedures in the future

## 4 Conclusions

This review has covered the chemistry of polyelectrolyte materials that are in the forefront to two major technical developments, namely environmentally acceptable industrial paints and improved medical and dental materials In both fields, external trends continue to drive developments in directions that favour polyelectrolytes Environmental legislation is making water-based paints increasingly attractive because they conform so readily to emission requirements, yet are presented to the user in the familiar way as liquids that dry out to give solid functional films

Polyelectrolyte biomedical materials, especially the glass-poly(alkenoates), are being used ever more widely as demand grows for materials that are biocompatible In dentistry, as an ageing world population tends to retain more of its teeth for longer, and also demands increasingly high standards in aesthetic tooth repair, polyelectrolytes are assuming greater importance In medicine surgical techniques for repair and replacement are becoming increasingly sophisticated, again fuelled by an ageing world population demanding higher standards Here, too, polyelectrolytes, through their blandness and compatibility with living tissue, have an increasingly important rôle to play

Both applications rely heavily on the contribution of chemistry Chemists, often working as part of interdisciplinary teams, and essential to provide the necessary new and exciting chemistry, will be central to continuing success in both fields

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